#### (19) World Intellectual Property Organization International Bureau



# 

#### (43) International Publication Date 18 July 2002 (18.07.2002)

#### **PCT**

#### (10) International Publication Number WO 02/055581 A3

(51) International Patent Classification7:

C08G 67/04

(21) International Application Number: PCT/US01/50462

(22) International Filing Date:

20 December 2001 (20.12.2001)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

60/257,911

21 December 2000 (21.12.2000) US

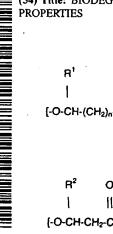
- (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): Jean-Philippe, Marie [FR/US]; 217 Hillcrest Drive, Wyoming, OH 45215 (US). MELIK, David, Harry

[US/US]; 4192 Intrepid Drive, Cincinnati, OH 45252 (US). SATKOWSKI, Michael, Matthew [US/US]; 613 Windingbrook Drive, Oxford, OH 45056 (US).

- (74) Common Representative: THE PROCTER & GAM-BLE COMPANY; c/o Mr. T. David Reed, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian

[Continued on next page]

## (54) Title: BIODEGRADABLE POLYHYDROXYALKANOATE COPOLYMERS HAVING IMPROVED CRYSTALLIZATION



**WO 02/055581** 

(57) Abstract: Compositions having improved crystallization properties and physical properties comprise (a) a continuous phase of first biodegradable polyhydroxyalkanoate comprising a copolymer, or a blend thereof, of at least two randomly repeating monomer units (RRMU), wherein the first RRMU has the structure (I): (I) wherein R1 is H, or C1 or C2 alkyl, and n is 1 or 2; and the second RRMU is different from the first RRMU and comprises at least one monomer selected from the group consisting of the structures (II) and (III): (II) wherein R2 is a C3-C19 alkyl or C3-C19 alkenyl, and (III) wherein m is from 2 to about 16, and wherein the copolymer has a melting point Tm1, and (b) a second crystallizable biodegradable polyhydroxyalkanoate homopolymer or copolymer, which comprises at least one randomly repeating monomer unit having the structure (IV): (IV) wherein R<sup>3</sup> is H, or C1 or C2 alkyl, and p is 1 or 2, and further wherein the second biodegradable polyhydroxyalkanoate has a melting point Tm2, wherein Tm2 is at least about 20°C greater than Tm1. The compositions are formed by solution or melt blending of the components (a) and (b) and may be formed into shaped articles.



patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

- with international search report

(88) Date of publication of the international search report: 17 April 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

0

### INTERNATIONAL SEARCH REPORT

nal Application No PCT/US 01/50462

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08L67/04

According to international Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included. In the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document with mobilities where appropriate, of	the relevant passages	Relevant to claim No.	
Y	US 5 693 389 A (LIGGAT JOHN JA 2 December 1997 (1997-12-02) cited in the application * the whole document *	1-10		
Υ	US 5 498 692 A (NODA ISAO) 12 March 1996 (1996-03-12) cited in the application * the whole document *	1-10		
Y	ORGAN, BARHAM: "Phase separate blend of poly(hydroxybutyrate) poly(hydroxybutyrate) poly(hydroxybutyrate) POLYMER, vol. 34, no. 3, 1993, pages 45 XP002207821 cited in the application * whole document *	1–10		
X Furth	er documents are listed in the continuation of box C.	Patent family members are listed	in annex.	
"A" documer consider filing de "L" documer which is citation "O" documer other m"P" documer later th.	nt which may throw doubts on priority claim(s) or s clied to establish the publication date of another or other special reason (as specified) int referring to an oral disclosure, use, exhibition or leans int published prior to the international filling date but an the priority date claimed	<ul> <li>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</li> <li>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</li> <li>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</li> <li>"&amp;" document member of the same patent family</li> </ul>		
Date of the a	ctual completion of the international search	Date of mailing of the International sea	erch report	
29 July 2002		16/08/2002		
Name and m	alling address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL – 2280 HV Rijswijk  Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,  Fax: (+31–70) 340–3016	Authorized officer  Marsitzky, D		

## INTERNATIONAL SEARCH REPORT

Intermedial Application No
PCT/US 01/50462

(Continua	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	PCT/US 01/50462
ategory °		Relevant to claim No.
1	WTHEY, HAY: "The effect of seeding on the crystallisation of poly(hydroxybutyrate) and co-poly(hydroxybutyrate-co-valerate)" POLYMER, vol. 40, 1999, pages 5147-5152, XP002207822 cited in the application * whole document *	1-10
E	WO 02 28969 A (AUTRAN JEAN PHILIPPE MARIE; PROCTER & GAMBLE (US)) 11 April 2002 (2002-04-11) * whole document *	1-10
		·
	·	
	0 (continuation of second sheet) (July 1992)	

### INTERNATIONAL SEARCH REPORT

Intermedial Application No PCT/US 01/50462

_						1 10402
	ent document in search report		Publication date		Patent family member(s)	Publication date
US !	5693389	Α	02-12-1997	AU	683466 B2	13-11-1997
				ΑU	6727594 A	20-12-1994
				CA	2162173 A1	08-12-1994
				EΡ	0700418 A1	13-03-1996
				FI	955645 A	23-11-1995
				WO	9428070 A1	08-12-1994
				JР	8510498 T	05-11-1996
				NO	954748 A	23-11-1995
US !	5498692	A	12-03-1996	US	5685756 A	11-11-1997
				US	5747584 A	05-05-1998
				AU	1056895 A	15-08-1995
				AU	730347 B2	08-03-2001
				AU	9820098 A	04-03-1999
				BR	9408512 A	04-03-1997
				CA	2181791 A1	03-08-1995
				CN	1142839 A	12-02-1997
				CZ	9602192 A3	11-12-1996
				EP	0739368 A1	30-10-1996
				FI	962997 A	26-07-1996
				HU	75180 A2	28-04-1997
				JP	9508423 T	26-08-1997
				NO	963104 A	27 <del>-</del> 09-1996
				NZ	276325 A	28 <b>-</b> 07-1998
				PL	315691 A1	25-11-1996
				RU	2137784 C1	20-09-1999
				SG	49114 A1	18-05-1998
				SK	97096 A3	09-04-1997
				TW	383316 B	01-03-2000
				WO	9520614 A1	03-08-1995
				US	RE36548 E	01-02-2000
				US	5489470 A	06-02-1996
				US	5602227 A	11-02-1997
				US	5618855 A	08-04-1997
				US	5780368 A	14-07-1998
				Z:A 	9500627 A	05-10-1995
WO	0228969	Α	11-04-2002	WO	0228969 A2	11-04-2002